Title
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Crystal structure of bis[(5-amino-1*H*-1,2,4-triazol-3-yl-κN^4)acetato-κO]diaquanickel(II) dihydrate

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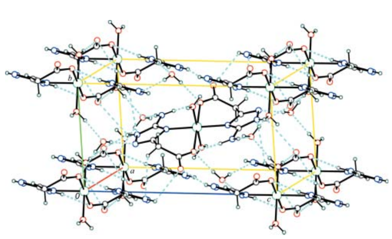
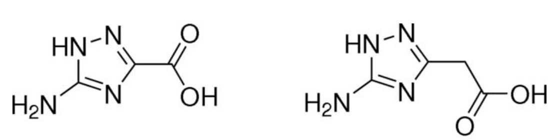
The title compound, $[Ni(C_4H_5N_4O_2)_2(H_2O)_2]\cdot 2H_2O$, represents the first transition metal complex of the novel chelating triazole ligand, 2-(5-amino-1*H*-1,2,4-triazol-3-yl)acetic acid (*ATAA*), to be structurally characterized. In the molecule of the title complex, the nickel(II) cation is located on an inversion centre and is coordinated by two water molecules in axial positions and two O and two N atoms from two *trans*-oriented chelating anions of the deprotonated *ATAA* ligand, forming a slightly distorted octahedron. The *trans* angles of the octahedron are all 180° due to the inversion symmetry of the molecule. The *cis*-angles are in the range 87.25 (8)–92.75 (8)°. The six-membered chelate ring adopts a slightly twisted boat conformation with puckering parameters Q = 0.542 (2) Å, Θ = 88.5 (2) and φ = 15.4 (3)°. The molecular conformation is stabilized by intramolecular N—H$\cdots$O hydrogen bonds between the amino group and the chelating carboxylate O atom of two *trans*-oriented ligands. In the crystal, the complex molecules and lattice water molecules are linked into a three-dimensional framework by an extensive network of N—H$\cdots$O, O—H$\cdots$O and O—H$\cdots$N hydrogen bonds.



1. Chemical context

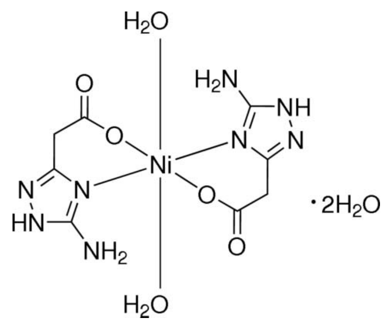
C-amino-1,2,4-triazoles are employed as polydentate ligands for the synthesis of coordination compounds with various metals that demonstrate useful spectroscopic, magnetic, biological and catalytic properties (Aromí *et al.*, 2011; Liu *et al.*, 2011; Gao *et al.*, 2013; Hernández-Gil *et al.*, 2014). Generally, aminotriazoles coordinate metals by either pyridine-type endocyclic nitrogen atoms or by the amino group (Aromí *et al.*, 2011; Liu *et al.*, 2011). Furthermore, aminotriazoles containing substituents with favorably oriented atoms bearing unshared electron pairs (N, S, O *etc.*) can act as chelating polydentate ligands (Biagini-Cingi *et al.*, 1994; Prins *et al.*, 1996; Ferrer *et al.*, 2004, 2012). 5-Amino-1*H*-1,2,4-triazole-3-carboxylic acid (*ATCA*, Fig. 1) was found to be a promising chelating ligand for which complexes with various metal cations have been reported recently (Chen *et al.*, 2011; Sun *et al.*, 2011; Wang *et al.*, 2011; Hernández-Gil *et al.*, 2012; Tseng *et al.*, 2014). In these complexes, metal cations are



ATCA ATAA

Figure 1
Structural formulas of 5-amino-1*H*-1,2,4-triazole-3-carboxylic acid (*ATCA*) and 2-(5-amino-1*H*-1,2,4-triazol-3-yl)acetic acid (*ATAA*).

chelated by the anions of *ATCA* owing to the formation of coordination bonds with nitrogen atoms of the triazole ring and the oxygen atom of the deprotonated carboxylic group.



In a continuation of our work on the synthesis and reactivity of aminotriazole carboxylic acids (Chernyshev *et al.*, 2006, 2009, 2010), we have focused our attention on another chelating ligand, namely 2-(5-amino-1*H*-1,2,4-triazol-3-yl)acetic acid (*ATAA*, Fig. 1), which can be considered as a homologue of *ATCA*. To the best of our knowledge, *ATAA* or its derivatives have not been studied previously for the synthesis of coordination compounds. Herein, we report the synthesis and crystal structure of an Ni^{II} complex of *ATAA*, the title compound $[Ni(C_4H_5N_4O_2)_2(H_2O)_2]\cdot 2H_2O$ (1).

2. Structural commentary

In the molecule of the title complex (1), the Ni^{II} cation is six-coordinated by two bidentate chelating ligands, anions of *ATAA*, and by two water molecules, forming a slightly distorted octahedron (Fig. 2). The *trans*-angles of the octahedron are all 180° due to the inversion symmetry of the complete molecule. The *cis*-angles are in the range 87.25 (8)–92.75 (8)°. The third water molecule is not involved in coordination. The anions of *ATAA* coordinate the Ni^{II} cation through the nitrogen atom N1 of the triazole ring and the oxygen atom O53 of the carboxylate group (Fig. 2), similarly to the complexes of *ATCA* with various metal cations (Chen *et al.*, 2011; Sun *et al.*, 2011; Wang *et al.*, 2011; Hernández-Gil *et al.*, 2012). The six-membered chelate ring adopts a slightly twisted boat conformation with puckering parameters of Q = 0.542 (2) Å, Θ = 88.5 (2), φ = 15.4 (3)°. The Ni—N1 bond length is 2.051 (2) Å, and the Ni—O1 and Ni—O53 bond lengths are 2.083 (2) and 2.059 (2) Å, respectively, within the normal ranges for other reported Ni^{II} complexes (Lenstra *et al.*, 1989; Virovets *et al.*, 2000; Bushuev *et al.*, 2002; Drozdzewski *et al.*, 2003; Fan *et al.*, 2010; Zheng *et al.*, 2011; Jin *et al.*, 2011). The aminotriazole fragment N1/C2/N3/N4/C5/N21 is planar (maximum deviation = 0.021 (3) Å for C2), its bond lengths and angles being analogous to complexes of *C*-amino-1,2,4-triazoles with transition metals (Ferrer *et al.*, 2004; Siddiqui *et al.*, 2011; Tabatabaee *et al.*, 2011). The bonds C2—N3 [1.330 (4) Å] and C5—N4 [1.304 (3) Å] are shorter than the bonds C2—N1 [1.342 (3) Å] and C5—N1 [1.365 (3) Å]. The molecular conformation is stabilized by intramolecular N21—H21*B*···O53 hydrogen bonds (Fig. 2, Table 1).

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N21—H21*A*···O2^{i}	0.83 (2)	2.04 (2)	2.876 (3)	176 (3)
N21—H21*B*···O53^{ii}	0.83 (2)	2.19 (2)	2.941 (3)	151 (3)
N3—H3···O54^{iii}	0.83 (3)	2.10 (3)	2.885 (3)	156 (3)
O1—H1*A*···O2^{iv}	0.82 (2)	1.92 (2)	2.739 (3)	176 (3)
O1—H1*B*···O54^{v}	0.82 (2)	1.96 (2)	2.780 (3)	173 (4)
O2—H2*A*···N4^{vi}	0.83 (2)	2.09 (2)	2.903 (3)	164 (3)
O2—H2*B*···O53^{vii}	0.83 (2)	1.98 (2)	2.811 (3)	176 (3)

Symmetry codes: (i) $x, y, z-1$; (ii) $-x, -y, -z$; (iii) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $x-\frac{1}{2}, -y-\frac{1}{2}, z-\frac{1}{2}$; (v) $-x-1, -y, -z$; (vi) $x+1, y, z+1$; (vii) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$.

3. Supramolecular features

In the crystal, molecules of the complex and lattice water molecules are linked into a three–dimensional framework by extensive N—H···O, O—H···O and O—H···N hydrogen bonds (Table 1, Fig. 3).

4. Database survey

More than twenty structures of chelate complexes of 3-substituted 5-amino-1,2,4-triazoles, in which N, O or S atoms

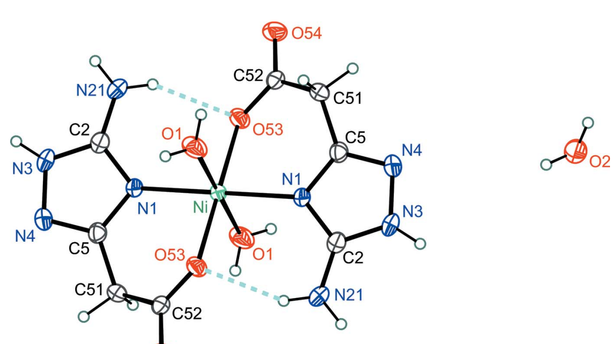


Figure 2
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. Intramolecular N—H···O hydrogen bonds are shown as dashed lines. Equivalent atoms are generated by symmetry code $-x, -y, -z$.

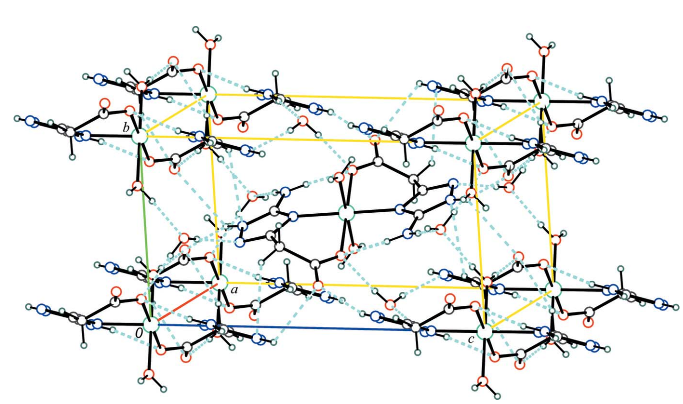


Figure 3
The crystal packing of the title compound viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

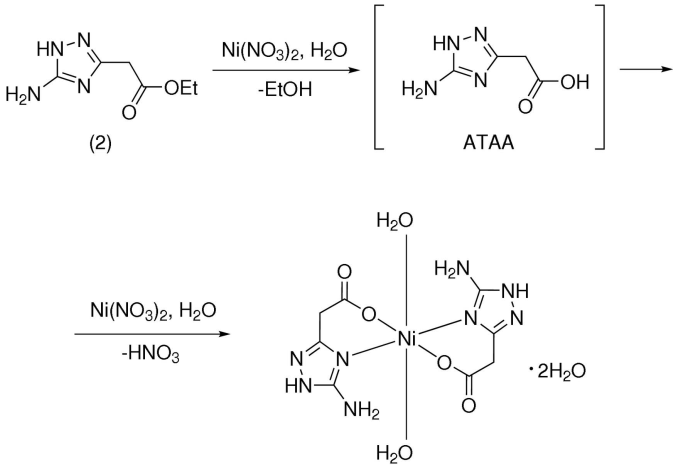


Figure 4
Reaction scheme showing the synthesis of the title compound (1).

of the substituent in the position 3 of the triazole ring play the role of a donor atom, were found in the Cambridge Structural Database (Version 5.35, November 2013 with 2 updates; Thomas *et al.*, 2010). The database reveals a total of seven structures of coordination compounds of 5-amino-1*H*-1,2,4-triazole-3-carboxylic acid (*ATCA*) with various metals (Chen *et al.*, 2011; Sun *et al.*, 2011; Wang *et al.*, 2011; Hernández-Gil *et al.*, 2012; Tseng *et al.*, 2014; Siddiqui *et al.*, 2011), six of which are chelate complexes. Coordination compounds of metals with the *ATAA* ligands or its derivatives were not found in the literature.

5. Synthesis and crystallization

All attempts to prepare crystals of complex (1) suitable for X-ray investigation by mixing solutions of *ATAA* or its sodium salt with solutions of Ni^{II} salts were unsuccessful and only microcrystalline precipitates of the sparingly soluble complex were obtained. Crystals of acceptable quality were prepared by slow hydrolysis of ethyl 2-(5-amino-1*H*-1,2,4-triazol-3-yl)acetate (2) in an aqueous solution of nickel nitrate (Fig. 4). A solution of 0.65 g (3.8 mmol) of compound (2) in water (10 ml) was added to a solution of 0.55 g, (1.9 mmol) of $Ni(NO_3)_2{\cdot}6H_2O$ in water (5 ml). After standing at room temperature for two weeks, the formed crystals were collected by filtration yielding the target compound (1).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. C-bound H atoms were placed in calculated positions with C—H = 0.97 Å for the CH_2 group and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$. The N,O-bound H atoms that are involved in hydrogen bonds were found from difference Fourier maps. Their distances to the parent atoms were refined to be equal, with a common $U_{iso}(H)$ value for pairs of related H atoms.

Table 2
Experimental details.

Crystal data	
Chemical formula	
M_r	412.99
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	295
a, b, c (Å)	7.6270 (17), 7.2603 (16), 13.580 (3)
β (°)	91.91 (2)
V (Å^3)	751.6 (3)
Z	2
Radiation type	Ag $K\alpha$, λ = 0.56085 Å
μ (mm^{-1})	0.72
Crystal size (mm)	0.20 × 0.20 × 0.20
Data collection	
Diffractometer	Enraf–Nonius CAD-4
Absorption correction	ψ scan (North *et al.*, 1968)
T_{min}, T_{max}	0.945, 0.958
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	1706, 1640, 1215
R_{int}	0.021
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.638
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.077, 1.02
No. of reflections	1640
No. of parameters	140
No. of restraints	3
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, −0.31

Computer programs: *CAD-4 EXPRESS* (Enraf–Nonius, 1994), *XCAD4* (Harms & Wocadlo, 1995), *SHELXS97* and *SHELXL2013* (Sheldrick, 2008), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012).

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References

Aromí, G., Barrios, L. A., Roubeau, O. & Gamez, P. (2011). *Coord. Chem. Rev.* **255**, 485–546.
Biagini-Cingi, M., Manotti-Lanfredi, A. M., Ugozzoli, F. & Haasnoot, J. G. (1994). *Inorg. Chim. Acta*, **227**, 181–184.
Bushuev, M. B., Virovets, A. V., Garcia, Y., Gieck, C., Sheludyakova, L. A., Ikorskii, V. N., Tremel, W., Gütlich, P. & Lavrenova, L. G. (2002). *Polyhedron*, **21**, 797–804.
Chen, Y.-C., Xu, J.-J., Wang, K.-B. & Wang, Y. (2011). *Chin. J. Struct. Chem.* **30**, 799–804.
Chernyshev, V. M., Chernysheva, A. V. & Starikova, Z. A. (2010). *Heterocycles*, **81**, 2291–2311.
Chernyshev, V. M., Chernysheva, A. V. & Taranushich, V. A. (2006). *Russ. J. Appl. Chem.* **79**, 783–786.
Chernyshev, V. M., Chernysheva, A. V. & Taranushich, V. A. (2009). *Russ. J. Appl. Chem.* **82**, 276–281.
Drożdżewski, P., Pawlak, B. & Głowiak, T. (2003). *Transition Met. Chem.* **28**, 727–731.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
Fan, R.-Z., Li, S.-J., Song, W.-D., Miao, D.-L. & Hu, S.-W. (2010). *Acta Cryst.* E**66**, m897–m898.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Ferrer, S., Ballesteros, R., Sambartolomé, A., González, M., Alzuet, G., Borrás, J. & Liu, M. (2004). *J. Inorg. Biochem.* **98**, 1436–1446.
Ferrer, S., Lloret, F., Pardo, E., Clemente-Juan, J. M., Liu-González, M. & García-Granda, S. (2012). *Inorg. Chem.* **51**, 985–1001.

Gao, J.-Y., Xiong, X.-H., Chen, C.-J., Xie, W.-P., Ran, X.-R. & Yue, S.-T. (2013). *Z. Anorg. Allg. Chem.* **639**, 582–586.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Hernández-Gil, J., Ferrer, S., Castiñeiras, A., Liu-González, M., Lloret, F., Ribes, Á., Coga, L., Bernecker, A. & Mareque-Rivas, J. C. (2014). *Inorg. Chem.* **53**, 578–593.
Hernández-Gil, J., Ferrer, S., Castiñeiras, A. & Lloret, F. (2012). *Inorg. Chem.* **51**, 9809–9819.
Jin, G.-H., Li, X., Hu, C. & Hu, L. (2011). *Acta Cryst.* E**67**, m988.
Lenstra, A. T. H., Slot, H. J. B., Beurskens, P. T., Haasnoot, J. G. & Reedijk, J. (1989). *Rec. Trav. Chim. Pays-Bas*, **108**, 133–138.
Liu, K., Shi, W. & Cheng, P. (2011). *Dalton Trans.* **40**, 8475–8490.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Prins, R., Biagini-Cingi, M., Drillon, M., de Graaff, R. A. G., Haasnoot, J., Manotti-Lanfredi, A.-M., Rabu, P., Reedijk, J. & Ugozzoli, F. (1996). *Inorg. Chim. Acta*, **248**, 35–44.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Siddiqui, K. A., Mehrotra, G. K., Narvi, S. S. & Butcher, R. J. (2011). *Inorg. Chem. Commun.* **14**, 814–817.
Sun, Y.-G., Xiong, G., Guo, M.-Y., Ding, F., Wang, L., Gao, E.-J., Zhu, M.-C. & Verpoort, F. (2011). *Z. Anorg. Allg. Chem.* **637**, 293–300.
Tabatabaee, M., Kukovec, B.-M. & Kazeroonizadeh, M. (2011). *Polyhedron*, **30**, 1114–1119.
Thomas, I. R., Bruno, I. J., Cole, J. C., Macrae, C. F., Pidcock, E. & Wood, P. A. (2010). *J. Appl. Cryst.* **43**, 362–366.
Tseng, T.-W., Luo, T.-T. & Lu, K.-H. (2014). *CrystEngComm*, **16**, 5516–5519.
Virovets, A. V., Bushuev, M. B. & Lavrenova, L. G. (2000). *J. Struct. Chem.* **41**, 717–720.
Wang, J., Li, W.-Z., Wang, J.-G. & Xiao, H.-P. (2011). *Z. Kristallogr. New Cryst. Struct.* **226**, 163–164.
Zheng, S., Cai, S., Fan, J. & Zhang, W. (2011). *Acta Cryst.* E**67**, m865.

supporting information

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Crystal structure of bis[(5-amino-1*H*-1,2,4-triazol-3-yl-κ*N*^{4})acetato-κ*O*]diaqua-nickel(II) dihydrate

Victor M. Chernyshev, Anna V. Chernysheva, Raisa S. Abagyan and Victor B. Rybakov

Computing details

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Bis[(5-amino-1*H*-1,2,4-triazol-3-yl-κ*N*^{4})acetato-κ*O*]diaquanickel(II) dihydrate

Crystal data

M_r = 412.99
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 7.6270 (17) Å
b = 7.2603 (16) Å
c = 13.580 (3) Å
β = 91.91 (2)°
V = 751.6 (3) Å^3
Z = 2
F(000) = 428
D_x = 1.825 Mg m^{-3}
Ag $K\alpha$ radiation, λ = 0.56085 Å
Cell parameters from 25 reflections
θ = 10.8–12.9°
μ = 0.72 mm^{-1}
T = 295 K
Prism, light green
0.20 × 0.20 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
non–profiled ω–scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.945, T_{max} = 0.958
1706 measured reflections
1640 independent reflections
1215 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 21.0°, θ_{min} = 2.4°
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 17$
1 standard reflections every 60 min
intensity decay: 1%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.077
S = 1.02
1640 reflections
140 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2 + 0.467P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R–factor wR and goodness of fit S are based on F^2, conventional R–factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R–factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R–factors based on F^2 are statistically about twice as large as those based on F, and R–factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Ni	0.0000	0.0000	0.0000	0.01840 (14)
N1	−0.0590 (3)	0.0113 (4)	−0.14834 (14)	0.0215 (5)
C2	0.0459 (3)	0.0087 (5)	−0.22579 (18)	0.0237 (5)
N21	0.2095 (3)	−0.0555 (4)	−0.22436 (19)	0.0380 (8)
H21A	0.278 (3)	−0.036 (5)	−0.2696 (17)	0.040 (7)*
H21B	0.248 (4)	−0.090 (5)	−0.1692 (15)	0.040 (7)*
N3	−0.0433 (3)	0.0713 (4)	−0.30469 (18)	0.0307 (6)
H3	−0.010 (4)	0.083 (4)	−0.362 (2)	0.029 (9)*
N4	−0.2124 (3)	0.1187 (4)	−0.28023 (17)	0.0289 (6)
C5	−0.2135 (4)	0.0798 (4)	−0.18651 (19)	0.0218 (6)
C51	−0.3727 (3)	0.1003 (4)	−0.12754 (19)	0.0242 (6)
H51A	−0.4200	−0.0215	−0.1160	0.029*
H51B	−0.4597	0.1678	−0.1668	0.029*
C52	−0.3496 (3)	0.1962 (4)	−0.02933 (19)	0.0206 (6)
O53	−0.2044 (2)	0.1806 (3)	0.01848 (14)	0.0248 (5)
O54	−0.4765 (3)	0.2802 (3)	0.00309 (17)	0.0335 (5)
O1	−0.1634 (3)	−0.2263 (3)	0.01911 (18)	0.0327 (5)
H1A	−0.129 (4)	−0.313 (3)	0.053 (2)	0.048 (8)*
H1B	−0.271 (2)	−0.238 (5)	0.017 (3)	0.048 (8)*
O2	0.4528 (3)	0.0268 (3)	0.62437 (15)	0.0320 (5)
H2A	0.556 (3)	0.054 (5)	0.641 (2)	0.039 (7)*
H2B	0.404 (4)	0.110 (4)	0.591 (2)	0.039 (7)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni	0.0162 (2)	0.0239 (3)	0.0150 (2)	0.0020 (2)	−0.00011 (16)	0.0011 (3)
N1	0.0180 (10)	0.0313 (13)	0.0150 (9)	0.0003 (12)	−0.0003 (8)	0.0021 (12)
C2	0.0253 (13)	0.0265 (14)	0.0193 (12)	−0.0005 (14)	0.0020 (10)	0.0020 (15)
N21	0.0282 (14)	0.063 (2)	0.0236 (13)	0.0098 (13)	0.0102 (10)	0.0131 (13)
N3	0.0322 (14)	0.0449 (16)	0.0152 (12)	0.0033 (12)	0.0051 (10)	0.0053 (11)
N4	0.0275 (13)	0.0400 (16)	0.0190 (12)	0.0058 (12)	−0.0017 (9)	0.0048 (11)
C5	0.0225 (13)	0.0246 (14)	0.0181 (13)	−0.0026 (12)	−0.0009 (11)	0.0006 (11)

C51	0.0161 (13)	0.0340 (17)	0.0224 (14)	0.0006 (12)	−0.0015 (11)	0.0017 (13)
C52	0.0202 (13)	0.0221 (14)	0.0196 (13)	0.0002 (11)	0.0032 (10)	0.0040 (11)
O53	0.0208 (10)	0.0322 (11)	0.0210 (10)	0.0049 (9)	−0.0042 (8)	−0.0041 (9)
O54	0.0238 (11)	0.0486 (13)	0.0282 (10)	0.0106 (10)	0.0032 (9)	−0.0058 (12)
O1	0.0202 (10)	0.0327 (13)	0.0448 (14)	−0.0046 (10)	−0.0041 (10)	0.0108 (11)
O2	0.0309 (11)	0.0371 (14)	0.0280 (11)	−0.0022 (11)	0.0007 (9)	0.0026 (11)

Geometric parameters (Å, º)

Ni—N1	2.051 (2)	N3—H3	0.83 (3)
Ni—N1^{i}	2.051 (2)	N4—C5	1.304 (3)
Ni—O53	2.0590 (19)	C5—C51	1.484 (4)
Ni—O53^{i}	2.0590 (19)	C51—C52	1.509 (4)
Ni—O1	2.083 (2)	C51—H51A	0.9700
Ni—O1^{i}	2.084 (2)	C51—H51B	0.9700
N1—C2	1.342 (3)	C52—O54	1.238 (3)
N1—C5	1.365 (3)	C52—O53	1.270 (3)
C2—N3	1.330 (4)	O1—H1A	0.822 (19)
C2—N21	1.332 (4)	O1—H1B	0.822 (19)
N21—H21A	0.834 (19)	O2—H2A	0.83 (2)
N21—H21B	0.834 (19)	O2—H2B	0.83 (2)
N3—N4	1.386 (3)		
N1—Ni—N1^{i}	180.0	H21A—N21—H21B	120 (3)
N1—Ni—O53	87.25 (8)	C2—N3—N4	110.3 (2)
N1^{i}—Ni—O53	92.75 (8)	C2—N3—H3	129 (2)
N1—Ni—O53^{i}	92.75 (8)	N4—N3—H3	121 (2)
N1^{i}—Ni—O53^{i}	87.25 (8)	C5—N4—N3	102.5 (2)
O53—Ni—O53^{i}	180.00 (13)	N4—C5—N1	114.6 (2)
N1—Ni—O1	92.36 (9)	N4—C5—C51	122.5 (2)
N1^{i}—Ni—O1	87.63 (9)	N1—C5—C51	122.9 (2)
O53—Ni—O1	91.63 (9)	C5—C51—C52	116.7 (2)
O53^{i}—Ni—O1	88.37 (9)	C5—C51—H51A	108.1
N1—Ni—O1^{i}	87.63 (9)	C52—C51—H51A	108.1
N1^{i}—Ni—O1^{i}	92.37 (9)	C5—C51—H51B	108.1
O53—Ni—O1^{i}	88.37 (9)	C52—C51—H51B	108.1
O53^{i}—Ni—O1^{i}	91.63 (9)	H51A—C51—H51B	107.3
O1—Ni—O1^{i}	180.0	O54—C52—O53	122.8 (3)
C2—N1—C5	103.7 (2)	O54—C52—C51	118.2 (2)
C2—N1—Ni	130.69 (17)	O53—C52—C51	119.0 (2)
C5—N1—Ni	123.09 (17)	C52—O53—Ni	130.20 (18)
N3—C2—N21	125.8 (2)	Ni—O1—H1A	120 (2)
N3—C2—N1	108.9 (2)	Ni—O1—H1B	132 (3)
N21—C2—N1	125.2 (2)	H1A—O1—H1B	104 (3)
C2—N21—H21A	123 (2)	H2A—O2—H2B	112 (3)
C2—N21—H21B	115 (2)		
C5—N1—C2—N3	−0.3 (3)	Ni—N1—C5—N4	163.8 (2)

Ni—N1—C2—N3	−162.2 (2)	C2—N1—C5—C51	177.4 (3)
C5—N1—C2—N21	−177.1 (3)	Ni—N1—C5—C51	−18.9 (4)
Ni—N1—C2—N21	21.0 (5)	N4—C5—C51—C52	−133.3 (3)
N21—C2—N3—N4	177.1 (3)	N1—C5—C51—C52	49.6 (4)
N1—C2—N3—N4	0.4 (4)	C5—C51—C52—O54	151.7 (3)
C2—N3—N4—C5	−0.2 (3)	C5—C51—C52—O53	−31.5 (4)
N3—N4—C5—N1	0.0 (3)	O54—C52—O53—Ni	162.5 (2)
N3—N4—C5—C51	−177.2 (3)	C51—C52—O53—Ni	−14.2 (4)
C2—N1—C5—N4	0.2 (4)		

Symmetry code: (i) −*x*, −*y*, −*z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N21—H21*A*···O2^{ii}	0.83 (2)	2.04 (2)	2.876 (3)	176 (3)
N21—H21*B*···O53^{i}	0.83 (2)	2.19 (2)	2.941 (3)	151 (3)
N3—H3···O54^{iii}	0.83 (3)	2.10 (3)	2.885 (3)	156 (3)
O1—H1*A*···O2^{iv}	0.82 (2)	1.92 (2)	2.739 (3)	176 (3)
O1—H1*B*···O54^{v}	0.82 (2)	1.96 (2)	2.780 (3)	173 (4)
O2—H2*A*···N4^{vi}	0.83 (2)	2.09 (2)	2.903 (3)	164 (3)
O2—H2*B*···O53^{vii}	0.83 (2)	1.98 (2)	2.811 (3)	176 (3)

Symmetry codes: (i) −*x*, −*y*, −*z*; (ii) *x*, *y*, *z*−1; (iii) *x*+1/2, −*y*+1/2, *z*−1/2; (iv) *x*−1/2, −*y*−1/2, *z*−1/2; (v) −*x*−1, −*y*, −*z*; (vi) *x*+1, *y*, *z*+1; (vii) *x*+1/2, −*y*+1/2, *z*+1/2.